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AQUATIC CHEMISTRY

Chemical Equilibria and Rates in Natural Waters

Third Edition

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9 $Fe^{2+}(aq) + H_2O_2 \rightarrow$	1.8	31	−116	Wells and Salam (1960)
10 $Fe^{2+} + FeOH^{2+} \rightarrow$	3.4 (21.6°C)	31	−75	Burgess (1978)
11 $Fe^{3+} + Cr^{2+} \rightarrow$	3.4	24	−117	Burgess (1978)
12 $FeOH^{2+} + Cr^{2+} \rightarrow$	6.5	22	−54	Burgess (1978)
13 $Co(NH_3)_5Cl^{2+} + Fe^{2+} \rightarrow$	−2.9	55	−126	Burgess (1978)
Dissociation:				
14 $H_2CO_3 \rightarrow CO_2 + H_2O$	1.2 s^{-1}	64	−15	Edsall (1969)

[a] 25°C, except as noted.
[b] $M^{-1}\ s^{-1}$, except for reaction 14, unimolecular, s^{-1}.
[c] Solvent exchange, formulated as second order, for first order, $k = k_{ex}55.6$, that is, $[H_2O] = 55$ M.

Reactions with larger $\Delta H^{\ddagger\circ}$ values are affected more strongly by temperature variation. For example, for $\Delta H^{\ddagger\circ} = 120$ kJ mol^{-1}, lowering temperature from 30°C to 5°C slows the rate by a factor of 70, whereas for $\Delta H^{\ddagger\circ} = 60$ kJ mol^{-1}, the same temperature change slows the rate by a factor of about 9.

Example 2.6. Hydration of CO_2 in Terms of Transition-State Parameters A reaction of importance in natural waters and biochemistry, the hydration of CO_2,

$$CO_2 + H_2O \rightarrow H_2CO_3$$

is described kinetically by the parameters $E_a = 63.0$, $\Delta H^{\ddagger\circ} = 60.5$ (kJ mol^{-1}), $\Delta S^{\ddagger\circ} = -107$ J K^{-1} mol^{-1}, and log $k_2 = -3.3$ ($M^{-1}\ s^{-1}$) at 25°C. The slowness of this reaction ($t_{1/2} \simeq 3$ min at 10°C) is associated with a large energy barrier as well as a highly negative activation entropy. The free energy of activation, $\Delta G^{\ddagger 0}$, is 92 kJ mol^{-1}, giving $K^{\ddagger} \simeq 10^{-16}$ M^{-1}, and indicating that the quasi-equilibrium concentration of the activated complex, $[H_2^{\ddagger}O, CO_2]^{\ddagger}$, for a 10^{-5} M CO_2 solution would be $\sim 10^{-19}$ M! For the corresponding *dehydration* reaction, $H_2CO_3 \rightarrow CO_2 + H_2O$, experimental values of the *unimolecular* rate constant vary from about 3 to 30 s^{-1} over the temperature range 5–30°C. Interpretation of these data in terms of ACT yields $\Delta H^{\ddagger\circ} = 61.5$ kJ mol^{-1} and $\Delta S^{\ddagger\circ} = -15$ J K^{-1} mol^{-1} for dehydration of H_2CO_3, consistent with $\Delta H^{\circ} = -1$ and $\Delta S^{\circ} = -92$ for the reversible *overall* reaction, and with an equilibrium constant, $K = k_f/k_b$, equal to the ratio of the hydration and dehydration rate constants, a consequence of the principle of detailed balancing (microscopic reversibility) (Moore and Pearson, 1981).

2.17. EQUILIBRIUM VERSUS STEADY STATE IN FLOW SYSTEMS

Open Flow Systems Versus Closed Systems

Most natural water systems are continuous, open systems. Flows of matter and energy occur in the real system. The time-invariant state of a continuous system with flows at the boundaries is the *steady state*.[†] This state may be poorly approximated by the *equilibrium* state of a closed system. In Figure 2.2 we indicated the important features of an open-system model with material fluxes and chemical reactions. The simple reversible reaction (a "model" reaction),

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

[†] The term *steady state* as used in this example means the time-invariant state of a flow system with chemical reactions. *Steady state*, with respect to chemical *mechanisms*, means that certain intermediates in a complex reaction are of low concentration, so that $dC/dt \simeq 0$. It is important to keep these usages of "steady state" distinct.

was introduced to illustrate elementary differences between closed- and op system models. Solution for the steady-state concentration values of A and gives the results

$$C_A = \frac{r\bar{C}_{A,0} + k_b(\bar{C}_{A,0} + \bar{C}_{B,0})}{k_f + k_b + r} \quad (13$$

$$C_B = \frac{r\bar{C}_{B,0} + k_f(\bar{C}_{A,0} + \bar{C}_{B,0})}{k_f + k_b + r} \quad (1$$

in which $r = Q/V$, the fluid flow rate constant (time^{-1}), and overbars den inflowing concentrations.

We examine the *ratio* of C_B and C_A and compare it with the ratio expec for chemical equilibrium. The ratio of C_B/C_A for the steady state is, divid equation 139 by equation 138,

$$\frac{C_B}{C_A} = \frac{r\bar{C}_{B,0} + k_f(\bar{C}_{A,0} + \bar{C}_{B,0})}{r\bar{C}_{A,0} - k_b(\bar{C}_{A,0} + \bar{C}_{B,0})} \quad (1$$

Equation (140) shows that C_B/C_A will tend toward k_f/k_b as the material f to the system becomes small, that is, as $r\bar{C}_{B,0}$ and $r\bar{C}_{A,0}$ vanish. For $r =$ the system becomes a closed system, and $C_B/C_A = k_f/k_b = K$, the equilibr constant. The quantity $r = Q/V$ is the reciprocal of the fluid residence tim of the well-mixed system: $r = \tau_R^{-1}$. As τ_R tends to very large values, the ste state concentrations of the system approach the equilibrium values.

A simple result is obtained when only A enters the system. Then, $\bar{C}_{B,}$ 0 and equation 140 reduces to

$$\frac{C_B}{C_A} = \frac{k_f\bar{C}_{A,0}}{r\bar{C}_{A,0} + k_b\bar{C}_{A,0}} = \frac{k_f}{r + k_b}$$

The steady-state concentration ratio quotient depends on the chemical rate stants and the flux rate constant. For $r \ll k_b$, $C_B/C_A \simeq k_f/k_b = K$; if $r \gg$ then $C_B/C_A \simeq k_f/r$. In terms of the residence time, τ_R, and the half-time o backward reaction, τ_b, the steady-state ratio approximates the equilibrium if $\tau_R \gg \tau_b$.

Example 2.7. Steady-State Composition of an Open Completely Mixed tem with the Reaction A ⇌ B as a Function of Residence Time Assume $\bar{C}_{B,0} = 0$, $k_f = 10^{-5}$ s^{-1}, and $k_b = 10^{-6}$ s^{-1}, so that $K = 10$. The resid time, τ_R, is varied over the range from 10^5 to 10^8 s. Table 2.10 shows calculated ratio of steady-state C_B/C_A to K for a 1000-fold variation in residence time relative to the characteristic reaction time ($\sim k_b^{-1}$).

The equilibrium assumption is justified for many reactions with short and long τ_R. Rate data for a large number of first- and second-order aqu

Table 2.9. Kinetic Parameters for Elementary Aqueous Reactions[a]

Reactants	$\log k^b$ (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\ddagger\circ}$ (J K^{-1} mol^{-1})	References

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Table 2.10. Composition[a] of a Completely Mixed Open System at Steady State for A $\underset{k_b}{\overset{k_f}{\rightleftharpoons}}$ B

τ_R (s)	r (s^{-1})	r/k_b	$\frac{C_B/C_A}{K}$
10^5	10^{-5}	10	0.09
2×10^5	5×10^{-6}	5	0.17
5×10^5	2×10^{-6}	2	0.33
10^6	1×10^{-6}	1	0.50
2×10^6	5×10^{-7}	0.5	0.67
5×10^6	2×10^{-7}	0.2	0.83
10^7	1×10^{-7}	0.1	0.91
10^8	1×10^{-8}	0.01	0.99

[a] $(C_B/C_A)/K$ versus τ_R; $k_f = 1 \times 10^{-5}\ s^{-1}$; $k_b = 1 \times 10^{-6}\ s^{-1}$.

reactions indicate τ_{chem} less than seconds to minutes, and many other aqueous reactions have τ_{chem} less than hours to days (Hoffmann, 1981). The residence times of a number of freshwater systems are greater than these ranges (Imboden and Lerman, 1979). Critical attention needs to be directed to slow chemical reactions for which $\tau_{chem} \gtrsim \tau_R$.

For many systems it is known that there exist regions or environments in which the time-invariant condition closely approaches equilibrium. The concept of local equilibrium is important in examining complex systems. Local equilibrium conditions are expected to develop, for example, for kinetically rapid species and phases at sediment–water interfaces in fresh, estuarine, and marine environments. In contrast, other local environments, such as the photosynthetically active surface regions of nearly all lakes and ocean waters and the biologically active regions of soil–water systems, are clearly far removed from total system equilibrium.

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